State of California

M E M O R A N D U M

To : Henry Voss, Director
Department of Food
& Agriculture
1220 N Street
Sacramento, CA 95814

Date : April 18, 1991

Subject : ARB Monitoring of
Telone

From : James D. Boyd
Executive Officer
Air Resources Board

In response to a Department of Food and Agriculture (DFA) request, the Air Resources Board (ARB) staff conducted ambient air monitoring for Telone (1,3-dichloropropene) resulting from its use as a pesticide. This request was made by the DFA pursuant to Division 7, Chapter 3, Article 1.5, Section 14021 of the Food and Agricultural Code. The monitoring results and additional background information are included in the enclosures to this memorandum.

The Telone monitoring was conducted in Merced County. Monitoring was conducted to coincide with anticipated Telone applications as a soil fumigant prior to planting sugarbeets and sweet potatoes. Several actions were taken to select possible sampling sites. These actions included meetings with DFA staff, discussions with representatives of the Agricultural Commissioner's Office of Merced County regarding the timing and location of anticipated applications, and surveys of possible monitoring locations. A chronology of these events has been included as Enclosure I.

Four locations were selected as sampling sites. A background site was selected in Merced. Twenty-four hour samples were collected four days each week from April 2 through May 4, 1990. A summary table of the monitoring results is presented in Enclosure II. The complete results are included in Enclosure III. Based on initial monitoring results which detected Telone concentrations which appeared to pose a significant risk to public health, DFA canceled all permits for Telone applications, pending further investigation. We are continuing to work with your staff on further studies, which most recently included the Imperial County test application by DowElanco in February during which we conducted monitoring. We will work with your staff and staff of the Department of Health Services (DHS) to evaluate data collected during this test application.

If you have questions regarding this submittal, please contact me or have your staff contact Genevieve Shiroma, Chief, Toxic Air Contaminant Identification Branch, at 322-7072.

cc: Dr. George Alexeeff, DHS
Dr. Donald Mengle, DHS
Jeff Palsgaard, Merced Co. APCO
Mike Tanner, Merced Co. Agricultural Commissioner
Steve Birdsall, Imperial Co. APCO/Agricultural Commissioner

Enclosures

Enclosures to the Transmittal Memorandum on
Telone Monitoring Data

April 1991

Enclosure I:	Chronology of Events
Enclosure II:	Summary Table
Enclosure III:	Report on Ambient Concentrations of Telone in Merced County

Enclosure I

Chronology of Events

Telone Monitoring
Chronology of Major Events

February 1990	DFA transmits to ARB monitoring recommendation for Telone.
March 1990	ARB prepares work plan for Telone sampling and analysis in Merced County.
March 1990	ARB staff discusses Telone use and sampling locations with representative of Merced County Agricultural Commissioner's Office.
April 2 - May 4, 1990	Sampling is conducted at Merced County sites.

Enclosure II

Summary Table

SUMMARY TABLE

Telone Pesticide Monitoring - Merced County[a)]
April - May 1990

Location	Number of 24-hour sampling periods	Number of samples above MDL[b)]	Maximum (ug/m^3)	Average[c)] (ug/m^3)
El Nido - Co. Fire Dept.	20	12	16.9[d)]	4.6
Dos Palos Y - Co. Fire Dept.	20	13	33.3	4.0
Stevinson - Merquin School	19	16	138.6	22.2
Hilmar - Jr. High School	20	14	160.7[d)]	24.5
Merced (background site)	20	9	3.2	0.8

[a)] Based on initial monitoring results, CDFA canceled all permits for Telone applications after two weeks of the five week monitoring period. The average concentrations reflect three weeks during which no applications occurred.

[b)] MDL (Minimum detection limit) = 0.1 ug/m^3 (0.02 ppb).

[c)] Average of samples above MDL.

[d)] Average of two collocated samples.

Enclosure III

Report on Ambient Concentrations of Telone
in Merced County

State of California

AIR RESOURCES BOARD

PESTICIDE MONITORING REPORT

Telone (1,3-dichloropropene) Monitoring in Merced County

Engineering Evaluation Branch

Monitoring and Laboratory Division

Test Report No. C90-014

Report Date: January 4, 1991

APPROVED:

_____, Project Engineer
Testing Section

_____, Manager
Testing Section

_____, Chief
Engineering Evaluation Branch

Telone Monitoring in Merced County

This report presents the results of ambient monitoring for the soil fumigant Telone (1,3-dichloropropene) at different locations in Merced County. The results are based on samples collected and analyzed by the Air Resources Board (ARB) staff using ARB test methods. The results have been reviewed by the staff and are believed to be accurate within the limits of the methods. However, data may have been affected by variables which were not apparent during the test, such as proximity of samplers to the plume after application of the fumigant.

Acknowledgments

The project engineer was Don Fitzell. The Instrument Technicians were Jack Rogers, Bud Thoma and Ken Lewis of the ARB. Assistance was provided by Lynn Baker of the ARB's Toxic Air Contaminant Identification Branch. Chemical analyses were performed by the ARB's Engineering and Evaluation Branch and Southern Laboratory Branch. Mike Poore of the Northern Laboratory Branch also provided confirmation of the fumigant as well as technical advice.

Information was provided by Loyd McCollum of the Merced County Department of Agriculture regarding the areas of Merced County where sugarbeets and sweet potatoes are grown and which were expected to receive applications of Telone. Assistance was also provided by Al Miguel of the Merced County APCD regarding the use of an APCD air monitoring station as a background site for this study.

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Telone Monitoring in Merced County

I. INTRODUCTION

At the request of the California Department of Food and Agriculture (CDFA) and the Air Resources Board (ARB) Toxic Air Contaminant Identification Branch, the ARB Engineering Evaluation Branch (EEB) conducted monitoring for Telone in Merced County during the months of April and May, 1990. This monitoring study was a coordinated effort between the ARB and CDFA in accordance with the requirements of Section 14022(c) of the Food and Agricultural Code, which requires the ARB "to document the level of airborne emissions" when requested by CDFA. The Merced County Office of the Agricultural Commissioner provided assistance regarding possible locations for the monitoring equipment near areas expected to receive applications of Telone.

II. PESTICIDE DESCRIPTION

Telone is a volatile, colorless to straw-colored liquid consisting of cis and trans isomers of the compound 1,3-dichloropropene. It has a molecular weight of 111.0, a boiling point of 103°C to 110°C and a solubility in water of approximately 2.3 gm/liter.

Telone is a restricted use pesticide under Title 3, California Code of Regulations, Section 6400. The EPA has classified it as a Class B-2 carcinogen (probable human carcinogen).

It is used on a wide variety of crops as a preplant soil treatment to control nematodes, fungi, insects, weeds and other soil pests. The CDFA Pesticide Use Report for 1988 reported statewide use of 16,518,814 pounds. Telone is injected into the soil, with application rates varying from 5 to 36 gallons per acre depending on the soil type and crop. In Merced County, Telone is used principally prior to planting sugarbeets and sweet potatoes.

III. SAMPLING LOCATIONS

The CDFA provided data which was used to determine areas of high usage and peak periods of application. This information was used to determine which locations would be expected to be near Telone applications.

The pesticide monitoring was conducted in Merced County at four ambient sites along with a fifth monitoring site (TABLE III.) in the City of

Merced designed to determine background concentrations. FIGURE I. shows the study area and the location of each of the monitoring sites. These sites were selected in accordance with the U.S. Environmental Protection Agency ambient monitoring siting criteria (see QA PLAN, APPENDIX V.)

IV. SAMPLING METHODOLOGY

The sampling method used during this study required passing measured quantities of ambient air through charcoal tubes (see APPENDIX I.). These tubes are 8mm x 110mm, coconut-base charcoal with 400 mg in the primary section with 200 mg in the secondary (SKC catalog #226-09). Any Telone present in the sampled ambient air is captured by the charcoal adsorbent contained in the tubes. Subsequent to sampling, the tubes were transported in an iced container to the ARB's Engineering Evaluation Branch in Sacramento and the Southern Laboratory Branch in El Monte for analysis.

Sampling trains designed to operate continuously were set up at the four sampling sites and one background site identified in FIGURE I. of this report. The sampling tubes were changed approximately every twenty-four hours.

Each sample train consisted of two charcoal tubes with tube covers, Teflon fittings and tubing, rain shield, flow meter, train support, and a 110 VAC vacuum pump. A diagram of the sampling train is shown in FIGURE II. On a daily basis, each tube was prepared for use by breaking off each sealed glass end and then immediately inserting the tube into a Teflon fitting. The tubes were oriented in the sampling train according to a small arrow printed on the side of each tube indicating the direction of flow. Covers were wrapped around the tube to protect the adsorbent from exposure to sunlight.

The sample pump was started and the flow through a rotameter adjusted with a metering valve to an indicated reading of 3.5 liters per minute (lpm). A leak check was performed by blocking off the sample inlet. The sampling train would be determined to be leak-free, if the indicated flow dropped to zero. Upon completion of a successful leak check, the indicated flow rate was again set at 3.5 lpm and was recorded (if different from the planned 3.5 lpm) along with date, time, and site location. Calibration prior to use in the field indicated that a flow rate of 3.0 lpm was actually achieved when the rotameters were set to 3.5 lpm.

At the end of each sampling period the final indicated flow rate (if different than the set 3.5 lpm), the stop date and time were recorded. The charcoal tubes were then removed from the sample train, end caps installed on both ends, and identification labels affixed to each tube. Each tube was then placed in a culture tube with a screw cap and stored with ice in a covered chest until the tubes were delivered to the appropriate laboratory for analysis.

V. ANALYTICAL METHODOLOGY

One of the two charcoal tubes recovered from each sampler was analyzed by the Engineering Evaluation Branch and the other by the Southern Laboratory Branch. Samples were analyzed independently and by different methods at each of the ARB's Laboratories involved. Engineering Evaluation Branch used carbon disulfide extraction, GC separation on a DB-624 column and measurement by Electron Capture Detector (APPENDIX II.). Southern Laboratory Branch used ethyl acetate/methanol extraction followed by GC separation on a DB-1 Megabore column and measurement by Hall Electroconductivity Detector. (APPENDIX III.)

Additionally, Northern Laboratory Branch (NLB) conducted confirmational analysis on select samples previously extracted by EEB. These samples were separated by GC on a DB-Wax column and measured by mass spectroscopy (APPENDIX IV.)

VI. RESULTS

A summary of the results are show in TABLE I. and the complete results in TABLE II. Because of a question regarding the relative proportions of the cis and trans isomer present in the calibration standard used, the individual counts generated by each isomer were combined and a single calibration curve used to determine concentrations. Using another standard in which the relative proportions of cis and trans were confirmed by GC/MS, indicated this made very little difference in the concentrations calculated. As can be seen from the Tables, there is excellent agreement between the two laboratories for most of the samples. The GC/MS confirmation by NLB is also in good agreement for the three samples measured, although somewhat lower.

As indicated by the data, Telone was detected at very significant levels. Even the site designated as background had measurable levels of Telone. After the confirmation by GC/MS analysis by Northern Laboratory Branch, ARB notified the Merced County Health Department and Board of Supervisors as required by Health and Safety Code Section 25180.7. This was followed by CDFA halting all permits for its use in the State of California on April 13, 1990. Monitoring was continued until the levels were consistently below 0.1 ug/m^3, the minimum detection limit (MDL).

VII. QUALITY ASSURANCE

Reproducibility, linearity, collection and extraction efficiency, minimum detection limit and storage stability were determined prior to sampling, as outlined in the S.O.P.'s for Telone (see APPENDIX II. and III.)

In addition, one field blank was prepared each week for analysis and one trip spike was prepared during the fourth week of sampling. The blank samples were all found to be at or less than the MDL. The spiked sample was measured at 0.84 ug (42.0% recovery) by EEB and 0.95 ug (48% recovery) by SLB. Some of the low yield might be attributed to slow evaporation of the standards over time, but does not account for the significant difference between this sample and extensive recovery studies conducted earlier. Because both laboratories consistently had similar results it is assumed that this single spiked value is in error and the recovery studies completed earlier represents the more realistic recovery values.

Because of the importance of this study, a complete Quality Assurance Audit (APPENDIX VI.) was conducted. This included a field audit as well as a system and an analytical audit of both laboratories involved.

TABLE I. SUMMARY OF TELONE MONITORING DATA

Engineering Evaluation Branch

Site[a]	Number of Samples[b]	Number above MDL[c]	Maximum Value (ug/m^3)	Second Maximum Value (ug/m^3)	Average (ug/m^3)
1.	20	9	3.2	1.2	0.8
2.	20	12	16.9[d]	9.0[d]	4.6
3.	20	13	33.3	4.9	4.0
4.	19	16	138.6	67.2	22.2
5.	20	14	160.7[d]	72.4	24.5

Southern Laboratory Branch

Site[a]	Number of Samples[b]	Number above MDL[c]	Maximum Value (ug/m^3)	Second Maximum Value (ug/m^3)	Average (ug/m^3)
1.	20	9	2.5	1.3	0.7
2.	20	12	17.0[d]	11.4[d]	5.0
3.	20	12	27.1	5.3	4.0
4.	19	15	145.7	54.6	21.1
5.	20	15	175.7[d]	51.4	21.9

[a] See TABLE III. and FIGURE I.

[b] Collocated samples counted as a single sample.

[c] MDL = 0.1 ug/m^3.

[d] Average of 2 collocated samples.

TABLE II. TELONE MONITORING DATA[a)]

Site[b)]	April 2-3 (ug/m^3)		April 3-4 (ug/m^3)		April 4-5 (ug/m^3)		April 5-6 (ug/m^3)	
	EEB	SLB	EEB	SLB	EEB	SLB	EEB	SLB
1.	3.2	2.5	1.2	1.3	0.8	0.9	0.6	0.4
2.	6.4	8.2	2.8	2.5	3.1	3.0	5.3	4.7
3.	2.0	2.1	0.3	0.3	2.3	2.3	2.9	2.6
4.	7.5	6.8	34.8*	36.0*	67.2	54.6	2.9	2.4
5.	13.8	17.9	145.1*	162.9*	6.5	6.6	46.9	36.1
5.[c)]	13.3	20.0	176.3*	188.5*	6.6	6.3	57.7	39.9

*NLB's GC/MS results for these three samples are: 4. = 28.5, 5. = 136.1 and 5.[c)]= 165.3 after correction for dilution and sampling volumes (see APPENDIX IV.)

Site[b)]	April 9-10 (ug/m^3)		April 10-11 (ug/m^3)		April 11-12 (ug/m^3)		April 12-13[d)] (ug/m^3)	
	EEB	SLB	EEB	SLB	EEB	SLB	EEB	SLB
1.	0.3	0.3	0.2	0.1	0.5	0.3	0.4	0.4
2.	8.2	11.1	2.8	2.6	7.3	7.5	16.2	16.4
2.[c)]	9.7	11.7	2.9	2.5	7.2	9.5	17.6	17.7
3.	33.3	27.1	2.2	3.9	2.6	1.8	4.9	5.3
4.	14.4	13.4	2.2	1.0	53.7	29.8	138.6	145.7
5.	72.4	51.4	6.0	6.6	10.3	7.5	15.3	17.4

Site[b)]	April 16-17 (ug/m^3)		April 17-18 (ug/m^3)		April 18-19 (ug/m^3)		April 19-20 (ug/m^3)	
	EEB	SLB	EEB	SLB	EEB	SLB	EEB	SLB
1.	0.2	0.2	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
2.	1.2	1.6	0.3	0.3	0.2	0.2	<0.1	<0.1
3.	1.3	1.7	0.1	<0.1	0.2	0.1	0.2	0.2
3.[c)]	1.4	1.8	0.1	<0.1	0.2	0.2	0.2	0.1
4.	14.6	16.5	5.8	6.0	8.5	10.7	3.3	3.3
5.	2.6	2.7	1.5	1.7	0.8	1.0	0.7	0.8

TABLE II. TELONE MONITORING DATA[a] (continued)

Site[b]	April 23-24[e] (ug/m^3)		April 24-25 (ug/m^3)		April 25-26 (ug/m^3)		April 26-27 (ug/m^3)	
	EEB	SLB	EEB	SLB	EEB	SLB	EEB	SLB
1.	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
2.	<0.1	<0.1	<0.1	<0.1	0.2	0.2	<0.1	<0.1
3.	<0.1	<0.1	0.1	0.1	<0.1	<0.1	<0.1	<0.1
4.	0.3	0.4	---[f]	---[f]	0.2	0.2	0.2	0.2
4.[c]	0.3	0.3	0.3	0.3	0.3	0.2	0.2	0.2
5.	<0.1	<0.1	0.2	0.2	<0.1	<0.1	0.1	0.2

Site[b]	April 30-May 1 (ug/m^3)		May 1-2 (ug/m^3)		May 2-3 (ug/m^3)		May 3-4 (ug/m^3)	
	EEB	SLB	EEB	SLB	EEB	SLB	EEB	SLB
1.	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
2.	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
3.	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
4.	<0.1	<0.1	<0.1	<0.1	---[f]	---[f]	<0.1	<0.1
4.[c]	<0.1	<0.1	<0.1	<0.1	---[f]	---[f]	<0.1	<0.1
5.	<0.1	<0.1	<0.1	0.1	<0.1	<0.1	<0.1	<0.1

EEB = Engineering Evaluation Branch, SLB = Southern Laboratory Branch.

Minimum detection limit = 0.1 ug/m^3.

[a] All samples are run overnight for 24 hours.

[b] See TABLE III. and FIGURE I.

[c] Duplicate collocated sample.

[d] Applications stopped on the afternoon of April 13.

[e] Rain on April 22 and 23.

[f] Sample run rejected.

TABLE III. MONITORING SITES

1. Merced (background site)
   Merced Co. APCD
   210 E. 15th St.

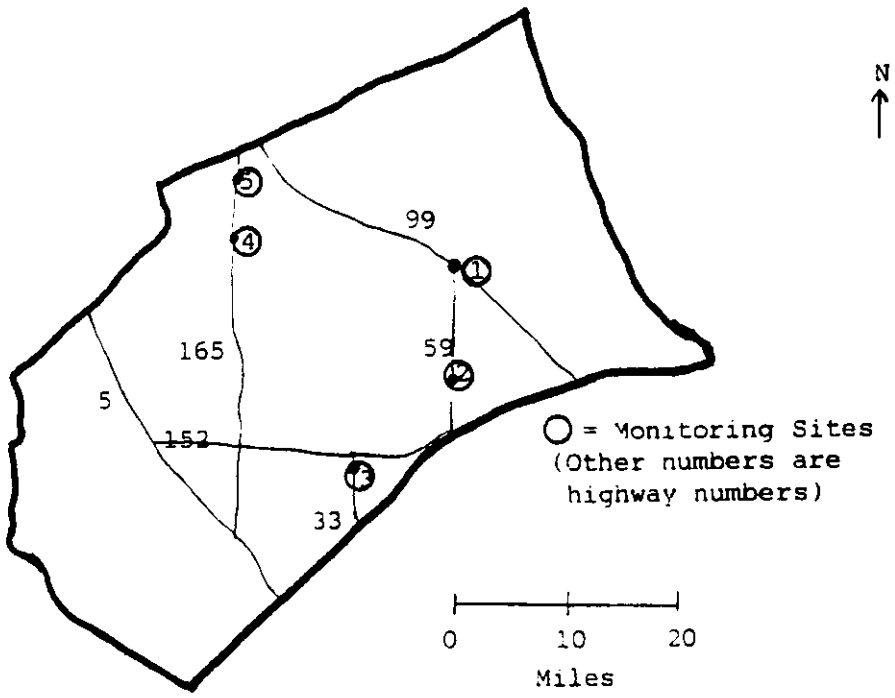
2. El Nido
   Merced Co. Fire Dept.
   10537 S. Highway 59 at El Nido Rd.

3. Dos Palos Y
   Merced Co. Fire Dept.
   8047 Dairy Ln. (Highway 33 just south of Highway 152)

4. Stevinson
   Merquin School
   Third Ave. west of Lander Ave. (Highway 165)

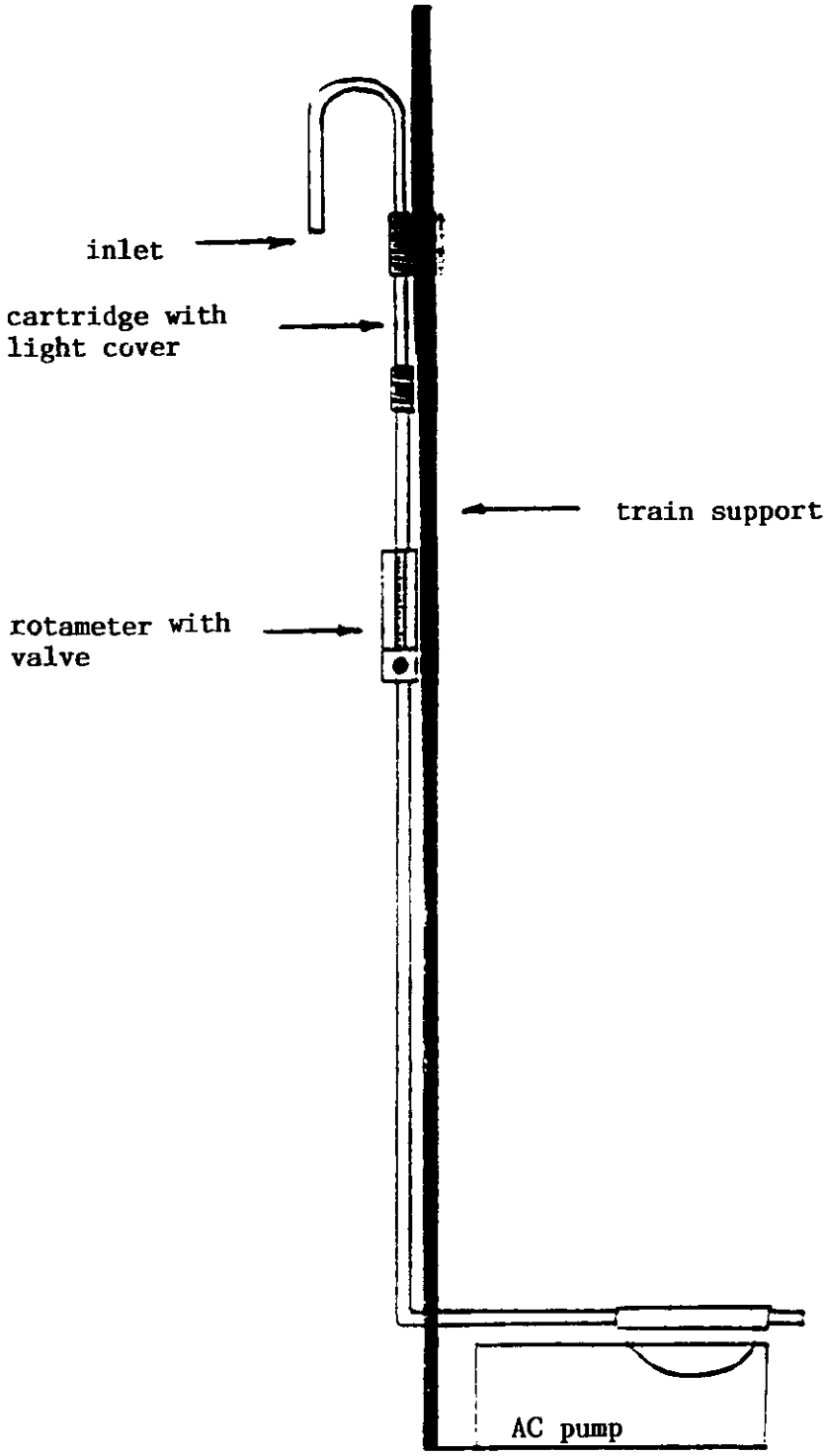
5. Hilmar
   Hilmar Jr. High School
   Lander Ave. north of Geer Ave.

FIGURE I. PESTICIDE MONITORING AREA



Merced County

FIGURE II. PESTICIDE SAMPLING APPARATUS



APPENDIX I. March 14, 1990

Telone Protocol C90-014

I. Introduction

At the request of the Department of Food and Agriculture (DFA), the Air Resources Board (ARB) will conduct a four week ambient monitoring program for Telone in Merced County. Monitoring is planned to begin the first week of April, 1990 and to continue for four weeks. Telone monitoring will be conducted in Merced County where it is used as a fumigant on a variety of crops. This is the area and season of peak application. A report on the measured concentrations will be submitted to DFA.

II. Sampling

Telone will be collected on charcoal tubes. Twenty-four hour samples will be collected with a flow rate of approximately 2 liters per minute.

Calibrated rotometers will be used to monitor sample flow rates. Samplers will be leak checked with the sampling media installed prior to and after each twenty-four hour sampling period. Flow rates will be allowed to stabilize before sampling begins and these rates will be recorded in a log book along with beginning and ending times. Any change in the flow rate at the end of the sampling period will also be noted.

Sampling will be conducted for four days per week at 3 sites in Merced County. Selection of monitoring sites will be based upon the siting criteria contained in the ARB Quality Assurance Plan for Pesticide Monitoring. Background samples will be collected at an appropriate monitoring site in Merced County. All samples will be stored in an ice chest until delivered to the laboratory for analysis.

III. Analysis

Analysis of samples will be by gas chromatography. The samples will be extracted with carbon disulfide, then injected into a gas chromatograph with an electron capture detector (ECD).

Quality control information will include: 1)recovery data from at least three samples spiked at three different concentrations, 2)instrument variability based on three replicate injections of a single sample at each of the three spiked concentrations, 3)stability study done with sets of triplicate spiked samples being stored under actual conditions and analyzed at appropriate intervals and 4)conversion/collection efficiency study conducted under field conditions (drawing ambient air through spiked samples at actual flow rates for the recommended sampling time) with three replicates at two spiked concentrations and a blank. Breakthrough studies will also be conducted to determine the capacity of the charcoal tubes.

IV. Quality Assurance

Quality assurance procedures for sampling and analysis will be followed as outlined in ARB's Quality Assurance Plan for Pesticide Monitoring. A rotating sampler will be used at each site to obtain duplicate samples in order to provide data for assessing precision. A chain of custody sheet will accompany all samples. Collection efficiency, stability, repoducibility and limit of detection studies will all be completed by the analytical laboratory prior to sampling. Field blanks will also be supplied to the laboratory.

APPENDIX II.

State of California
Air Resources Board
Monitoring and Laboratory Division/EEB

Standard Operating Procedure for the Analysis of
Telone (1,3-dichloropropene) in Ambient Air

1. SCOPE

This is a gas chromatography/electron capture method for the determination of 1,3-dichloropropene from ambient air samples. The method was adapted from NIOSH Method 1003 (Issued 2/14/84.).

2. SUMMARY OF METHOD

The exposed charcoal tubes are stored in an ice chest or refrigerator until desorbed with 3 ml of carbon disulfide. The injection volume is 2 ul. A gas chromatograph with an electron capture detector is used for analysis.

3. INTERFERENCES/LIMITATIONS

Method interferences may be caused by contaminants in solvents, reagents, glassware and other processing apparatus that can lead to discrete artifacts or elevated baselines. A method blank must be done with each batch of samples to detect any possible method interferences.

4. EQUIPMENT AND CONDITIONS

A. INSTRUMENTATION:
Varian 3400 gas chromatograph
Varian 604 Data System

Detector: 350°C

Injector: 250°C
Column : J&W Scientific DB-624, 30 meter, 0.32 mm i.d., 1.0 um film thickness.

Program: Initial 40°C, hold 1 min.; to 70°C @ 50°C/ min., hold 1 min.; to 85°C @ 1°C/min., hold 0.0 min.; to 200°C @ 30°C/min., hold 5 min.

Splitter open @ 0.8 min.

Flows:

column: He, 30 cm/sec.
make up: N_2, 40 ml/min.
splitter: 44 ml/min.

B. AUXILIARY APPARATUS:

1. Glass amber vials, 4 ml capacity with septum caps.
2. Vial Shaker, SKC, or equiv.

C. REAGENTS

1. Carbon Disulfide, ACS Grade, or better
2. Telone (cis-1,3-dichloropropene and trans-1,3-dichloropropene mixture), Chem Service PS-152, 99+%, or equiv.

5. ANALYSIS OF SAMPLES

1. It is necessary to analyze a solvent blank with each batch of samples. The blank must be free of interferences. A solvent blank must be analyzed after any sample which results in possible carry-over contamination.

2. At least one calibration sample must be analyzed for each batch of ten samples. The response of the standard must be within 10 % of previous calibration analyses.

3. Carefully score the primary section end of the sampled charcoal tube above the retainer spring and break at the score. Remove the glass wool plug from the primary end of the charcoal tube with forceps and place it into a 4 ml amber colored sample vial. Pour the charcoal into the vial and carefully add 3.0 ml carbon disulfide. CAUTION: HEAT WILL BE GENERATED. Seal the vial.

Retain the secondary section of the charcoal tube for later analysis to check the possibility of breakthrough.

4. Place the sample vial on a desorption vibrator for 45 minutes. Remove the carbon disulfide extract and store in a second vial at $4^{o}C$ until analysis.

5. After calibration of the GC system, inject 2.0 ul of the extract. If the resultant peaks for telone have a measured area greater than that of the highest standard injected, dilute the sample and re-inject.

6. Calculate the concentration in ug/ml based on the data system calibration response factors. If the sample has been diluted, multiply the calculated concentration by the dilution factor.

7. The atmospheric concentration is calculated according to:

Conc., ug/m^3 = (Extract Conc., ug/ml X 3 ml) / Air Volume Sampled, m^3

6. QUALITY ASSURANCE

A. Instrument Reproducibility

Triplicate injections of 3 standards at three different concentrations were made to establish the reproducibility of this instrument. This data is shown in TABLE 1.

TABLE 1. INSTRUMENT REPRODUCIBILITY

AMOUNT INJECTED (ug/ml)		INTEGRETATION COUNTS			
trans	cis	trans	(%)	cis	(%)
0.024	0.076	15,099 ± 209	(±1%)	10,808 ± 178	(±2%)
0.24	0.76	141,742 ± 3,675	(±3%)	96,384 ± 1,939	(±2%)
2.4	7.6	1,716,441 ± 28,757	(±2%)	1,372,607 ± 41,371	(±3%)

B. Linearity

A five point calibration curve was made ranging from 0.05 ug/ml to 10.0 ug/ml. The coresponding equation and correlation coefficient is:

total (cis + trans) $y = 3.173 \times 10^{-6} X + 0.0650$ Corr. = .9991

The standard deviation of these values based on triplicate injections was <3% for each concentration.

C. Minimum Detection Limit

Using the equation above and the data below, the minimum detection limit for Telone was calculated by:

$$MDL = |i| + 3(s.d._{low})$$

where : $|i|$ = the absolute value of the intercept of the standard curve (from above).

$s.d._{low}$ = the standard deviation of the lowest concentration used for the standard curve.

lowest concentration used = 0.05 + 0.001 ug/ml

$MDL = |0.0650| + 3(0.001) = 0.068$ ug/ml

Using 3 ml extraction volume and an average of 4.3 m^3 sample volume:

$$\frac{0.068 \text{ ug/ml} \times 3 \text{ ml}}{4.3 \text{ m}^3} = 0.05 \text{ ug/m}^3$$

Because of the high sensitivity, a MDL of 0.1 ug/m^3 is recommended to insure reliability of the data.

D. Collection and Extraction Efficiency (Recovery)

Collection and extraction efficiency data for Telone on charcoal is presented in TABLE 2. Note that no breakthrough occurred at the levels tested.

TABLE 2. COLLECTION AND EXTRACTION EFFICIENCY FOR TELONE ON CHARCOAL

CIS			TRANS			TOTAL		
Amount Spiked (ug)	Amount Recovered (ug)	(%)	Amount Spiked (ug)	Amount Recovered (ug)	(%)	Amount Spiked (ug)	Amount Recovered (ug)	(%)
0.76	0.63 ± 0.07	(83)	0.24	0.27 ± 0.02	(113)	1.0	0.90 ± 0.08	(90)
7.6	7.8 ± 0.3	(103)	2.4	2.0 ± 0.1	(83)	10.0	9.8 ± 0.3	(98)
15.2	14.8 ± 2.2	(97)	4.8	4.4 ± 0.8	(92)	20.0	19.2 ± 3.0	(96)
30.4	25.5 ± 0.7	(84)	9.6	8.8 ± 0.2	(92)	40.0	34.3 ± 0.9	(86)

* Amount spiked on to primary section of charcoal tube. The tube was then subjected to an air flow of approximately 3 lpm for 24 hours. The primary and secondary sections were then desorbed with 3.0 ml of carbon disulfide and analyzed by capillary column GC/ECD. No Telone was found in the secondary charcoal section.

E. Storage Stability

Storage stability studies were done in triplicate for 1.0 ug telone spikes on charcoal tube primary sections over a period of 38 days. The percent recovery data for storage stability is presented in TABLE 3.

TABLE 3. TELONE STORAGE STABILITY AT $4^{o}C$

AMOUNT SPIKED (cis + trans)	PERCENT RECOVERY				
	1 DAY	3 DAYS	5 DAYS	11 DAYS	38 DAYS
1.0 ug	93 ± 8	71 ± 11	72 ± 5	76 ± 5	66 ± 4

APPENDIX III.

State of California
Air Resources Board
Monitoring and Laboratory Division
Organics Analysis Section/SLB

S.O.P. No. SLB111

Standard Operating Procedure for the Determination of 1,3-Dichloropropene (Telone) from Ambient Air Samples Collected on a Coconut Charcoal Adsorption Tube Using a Gas Chromatograph/Hall Detector Combination

INTRODUCTION

A laboratory analysis procedure for the determination of the pesticide 1,3-Dichloropropene (Telone) was developed to assess the amounts present in ambient air field samples collected on adsorbent tubes with a coconut charcoal substrate. The field samples were collected at locations downwind from its point of application by ARB/MLD/Engineering Evaluation Branch (project C90-014) in the San Joaquin Valley. There was no method covering the analysis of Telone by ARB/MLD/SLB; therefore, a new procedure was developed. Ethyl acetate, a general extraction solvent used for chlorinated pesticides, was used in this analysis with up to 20% methanol added to increase the extraction efficiency at low collection levels. Both the cis- and the trans- forms of the pesticide were quantitated using gas chromatography. Additional selectivity for the chlorinated pesticide was obtained by using a Hall Detector operating in the halogen mode. Subsequent to the completion of the test samples, and before the finalization of the project, modifications to the procedure were made by adding a second GC column and ECD detector for simultaneous analysis of the analytes; this revised procedure will be covered in Revision #1. All extraction operations were performed in a ventilation hood and suitable hand and body protection were worn.

1.0 SCOPE

1.1 This method covers the determination of 1,3-dichloro-propene collected from ambient air with coconut charcoal adsorbent tubes in the range from 0.1 to 200 micrograms. The method has the advantage of being selective for halogenates, rapid, suitable for automated analysis, and can be applied to other chlorinated compounds that elute from the GC column, but is limited to the cis- and trans- forms of this compound.

1.2 This method is restricted to those halogenated pesticides that are efficiently extractible from coconut charcoal using ethyl acetate or a solvent mixture containing mostly ethyl acetate, that can be

eluted with no interferences from the GC column, and that can be detected with a Hall conductiometric detector.

1.3 No interferences were tested for, and none were apparent during the sample analysis.

2.0 PHYSICAL PROPERTIES AND RELATED INFORMATION

2.1 CAS Registry No: 542-75-6
2.2 Molecular Weight: 111.0
2.3 Boiling Point: 108C
2.4 Color: Colorless-to-Amber Liquid
2.5 Specific Gravity: 1.220 at 20C
2.6 Molecular Formula: C3H4Cl2
2.7 Vapor Pressure: 3.7 kPa at 20C
2.8 Solubility: 1 g/l in water at 20C; miscible with hydrocarbons, halogenated solvents, esters and ketones.
2.9 Mode of Action: Soil fumigant nematicide, secondary insecticide and fungicide for fruits, vegetables and other field crops.
2.11 Degradation: In soil, undergoes hydrolysis to the corresponding 3-chloroallyl alcohols.

3.0 REFERENCES

3.1 "The Agrochemicals Handbook, Second Edition", The Royal Society of Chemistry, Information Services, Thomas Graham House, Science Park, Milton Road, Cambridge CB4 4WF England

3.2 Mitchell, G.D., "Trace Gas Calibration Systems Using Permeation Devices," in Sampling and Calibration for Atmospheric Measurements, ASTM STP 957, J.K. Taylor, Ed., American Society for Testing and Materials, 1987, pp 110-120.

4.0 ANALYTICAL PARAMETERS

4.1 Limit of Detection for the Analysis - The detection limit of the analytical procedure is 0.2 ng/ul per injection. This is the concentration of 1,3-dichloropropene in solution (either cis-form or trans-form) that will give a GC peak whose area is approximately the sum of the zero offset of the calibration curve and three times the zero noise using a second order, least squares fit to the calibration data, and is an average of the values for the cis- and trans-Telone.

4.2 Limit of Detection for the Procedure - The detection limit of the overall procedure is 0.6 ug per sample. This is the amount of 1,3-dichloropropene spiked on the adsorbent tube that allows the recovery of an amount of Telone equivalent to the detection limit of the analytical procedure assuming an extraction efficiency of 100%.

4.3 Instrument Response - The instrument response over the concentration range of 0.2 to 100 ng/ul for Telone is nonlinear. The

degree of nonlinearity is such that response factor quantitation at 10 ng/ul will result in an underestimate of the concentration at a level of 100 ng/ul.

4.4 Precision - The short term precision of the analytical procedure is ± 5% at an analyte concentration of 2 ng/ul based on the analysis of 10 samples consecutively. The long term precision (for multiple samples) is ± 15% based on the variability in the analysis of control samples. Factors such as prior sample analysis and detector conditioning were found to affect the sensitivity of the Hall detector for some analyses

5.0 ADSORBENT TUBE PARAMETERS

5.1 Breakthrough - The breakthru concentration was found to be higher than 60 ug, at a flow rate of 3 l/min for 24 hours based on the spiking of charcoal tubes with 60 ug of material using a permeation tube.

5.2 Desorption Efficiency - The efficiency with which 1,3-dichloropropene can be desorbed from coconut charcoal adsorbent tubes used to collect 1,3-dichloropropene at a flow rate of 3 l/min for 24 hours was found to be 80%. This value was determined using a permeation tube with trans-1,3-dichloropropene operating a known emission rates.

5.3 Interferences - Interferences would consist of any halogenated hydrocarbons that are extractable from blank adsorbent tubes and coelute with Telone from the GC column. No significant interferences were inferred from the chromatograms of the samples, although lower boiling halogenated materials were detected in extracted, ambient air samples.

6.0 ANALYTICAL PROCEDURE

6.1 Equipment and Apparatus

6.1.1 Gas Chromatograph - A model 6000 gas chromatograph equipped with a model AS-8000 AutoSampler (Varian Instruments, Inc.).

6.1.2 GC Column - A DB-1 fused silica cappillary column with a film thickness of 3.0u, 30M length, 0.53mm diameter, (J+W Scientific PN 125-1034 or equivalent)

6.1.3 Detector - A model 700A Hall electrolytic conductivity detector operating in the halogen mode (Tracor Instruments, Analytical Division).

6.1.4 Data Handling - The GC peaks were integrated with a Vista 402 GC Data System. The nonlinear concentration profile required off-line calculations; a PC computer and a Lotus 1-2-3 (version

2. 2) spreadsheet program were used.

6.2 Instrument Conditions:

6.2.1 Column He flow - 7.0 cc/min
6.2.2 Column oven temperature - 50C
6.2.3 Injector temperature - 220C
6.2.4 Detector temperature - 220C
6.2.5 Injection volume - 1.0ul

6.3 Detector Conditions:

6.3.1 Reactor temperature setting - 800C
6.3.2 Reactor base temperature - 220C
6.3.3 Reactor Gas flow - 50 cc/min hydrogen, Hall grade
6.3.4 Reactor makeup gas flow - 19.5 cc/min Helium
6.3.5 Detector solvent - Propanol at 0.5-1.0 cc/min

6.4 Desorption vials - Glass vials, 4ml, with Teflon-coated rubber septums and screw caps. Precleaned for pesticide analysis.

6.5 Sample shaker/desorber with timer and sample racks.

6.6 AutoSampler Vials - Glass Autosampler vials, 1.5ml, with Teflon coated septum and screw caps; to fit Varian Model AS-8000 Autosampler.

6.7 Volumetric Flasks - Class A glassware; 10ml, 25ml, 50ml, and 100ml.

6.8 Volumetric Syringes - Class A syringes; 10ul, 100ul and 1000ul.

6.9 Sample filter - Syringeless 0.45u, PTFE membrane sample filter (Gelman Acroprep filter or equivalent).

6.10 Sample Tubes - Sorbent sample tube with coconut charcoal substrate; 400mg primary section, 200mg backup section (SKC, Inc. #226-09 or equivalent). All adsorbent tubes used for analytical development should be selected from the same manufacturing batch as the field sampling tubes.

6.11 Reagents and Materials

6.11.1 Purity of Reagents - Pesticide grade chemicals shall be used in all extractions and reagent grade chemicals should be used at other times. It is intended that these should conform to specifications of the American Chemical Society.

6.11.2 Ethyl acetate - Pesticide residue analysis grade (Baker Analyzed Reagent); desorbent solvent.

6.11.3 Methyl alcohol - Pesticide residue analysis grade (Baker Analyzed Reagent); desorbent solvent.

6.11.4 Desorbent solvent - Ethyl acetate blended with up to 20% (vol/vol) methyl alcohol. The same solvent composition should be used in all solution preparation.

6.11.5 Telone (1,3-Dichloropropene) - Mixture of the cis and trans isomers (50%/50%); Certified stock standard, 1000 ng/ul (accuracy of 0.5% by volume) in toluene or ethyl acetate (Nanogens, Inc.).

6.11.6 Tetrachloroethene - Reference compound, 1000 ng/ul in ethyl acetate; diluted to 1 ng/ul in calibration solutions (Aldrich Chemical). This compound was used for qualitative confirmation of the calibration accuracy.

6.12 Standards Preparation - Prepare a 100 ng/ul calibration solution from a 1000 ug/cc standard (0.5% certified standard of a 50/50 mixture of cis/trans Telone, Nanogens, Inc.) by diluting with an 80/20 mixture of ethyl acetate/methanol. Subsequent dilutions to 0.5, 1.0, 2.0, 4.0, 10.0, 25.0, and 50.0 ng/ul can be made from this solution.

6.13 Sample Preparation

6.13.1 Remove the end caps of the sorbant tube, score the tube above the location of the retainer ring, and break the tube. Remove glass-wool plug from primary end (inlet) of the charcoal sorbent tubes with forceps and transfer to a 4ml extraction vial. Pour the charcoal from the primary section (400 mg end) into the vial.

6.13.2 Add 3.0ml of extract/desorbent solvent. Seal vial securely with Teflon side of cap gasket facing the solution.

6.13.3 Remove foam separator plug of the charcoal sorbent tube with forceps and transfer to a 4ml extraction vial. Pour the charcoal from the secondary section into the vial. Remove the final foam plug with forceps and place in the vial.

6.13.4 Add 3.0ml of extract/desorbent solvent to the vial containing the secondary section (200mg end). Seal vial securely with Teflon face of cap gasket facing solution. Note: this section can be extracted, stored and then analyzed only if the primary section shows a positive result.

6.14 Sample Extraction

6.14.1 Place sealed vials into sample shaker racks and agitate for 60 minutes.

6.14.2 Separate the solvent from the charcoal by filtering the extracts through 0.45u, PTFE filters into sample storage vials.

6.14.3 Place about 1.5 cc of the filtrate into prelabeled, Autosampler vials and seal cap with Teflon face of septum toward the filtrate solution. Fill all vials with the same volume of filtrate.

6.14.4 Separate the unused portions of the filtrates, place in a vial, and store in a freezer until needed or for a maximum of one year after the report has been isssued. Do not store filtrate and spent adsorbent together.

6.15 Quality Control - A multipoint calibration with a set of five to eight standards are analyzed with each set of samples. One of these concentrations is 2.0 ng/ul, which is used to normalize the instrumental response curve on a daily basis. Control samples are included after every fourth sample tested.

6.16 Analysis - Place the extracted samples into the GC autosampler for analysis. Determine the area counts using suitable electronic integration for each of the 1,3-dichloropropene peaks and compared these to the standard calibration curve.

6.17 Instrumental Response Curves - The measured responses for the calibration solutions are used to prepare a calibration curve. A linear regression of a log-log plot of area counts vs concentration (or an equivalent procedure) is used to determine the non-linear instrument response curve from the calibration data. A standard normalized curve was developed using the following average regression parameters.

	cis-Telone	trans-Telone
slope:	1.0736	1.1422
intercept:	4.0702	4.0115

A multiplicative factor is calculated from the daily calibration results by using the area count for the calibration solution at 2.0ng/ul for both the cis- and trans-telone analyses and ratioing these to the area counts for the standard curve.

FACTOR=(Area Cts-ref. curve)/(Area Cts-daily calib.)

6.18 Calculations - The concentrations (ng/ul) of the extracted test solutions are calculated from the instrument response curve using the slope, intercept and normalization constants as follows:

Log(Conc) = log<(FACTOR)*(Area Counts) - (Intercept)/(Slope)>

The data analysis program is set up to report the results in units of ng/ul.

6.18 Interferences - Any compound with the same general retention times as the analyts and which also gives a significant detector

response is a potential interference. GC parameters may be changed to circumvent interferences. It is recommended that other procedures (such as GC/MS) be used to confirm samples purity whenever possible.

6.20 Safety Precautions - All extractions and sample preparations should be carried out in a ventilated hood, and suitable hand and body protection should be worn.

7.0 SUPPORTING DATA

7.1 Limit of Detection Determination

7.1.1 The Limit of Detection (LOD) was calculated using a second order algorithm to fit the data,

$$Conc = a*X2 + b*X * c$$

and the equation for determining the LOD becomes the following.

$$LOD = |c|/b + 3*s/b$$

7.1.2 The average limit of detection (LOD) for cis- and trans-1,3-Dichloropropene calculated from the values in the table is 0.2 ng/ul.

7.1.3 Table of data used in the Calculation of the Limit of Detection.

Table 7-1. Limits of Detection for the Hall Detector.

	cis 1,3-dichloropropene		trans 1,3-dichloropropene	
Concentration (ng/ul)	Calibration Date-4/16/90 (area counts)	Calibration Date-5/16/90 (area counts)	Calibration Date-4/16/90 (area counts)	Calibration Date-5/16/90 (area counts)
0.05	346	3020	402	2677
0.25	2722	8426	2414	7407
0.50	4331	13847	3596	12329
1.00	11544	29603	10183	26660
2.00	25180	64112	22855	58485
4.00	47355	130641	44139	122365
10.00	142647	314858	147606	310579
25.00	370215	778792	411001	805597
Coefficient				
a	13656	31968	13274	30437
b	50.23	-32.82	132.4	73.92
c	-2202	-55.97	-3100	-1471.7
s*	8	756	20	700
Calculated LOD	0.16 ng/ul	0.07 ng/ul	0.23 ng/ul	0.12 ng/ul

* Standard deviation calculated from two measurements.

7.2 Determination of Instrument Reproducibility

7.2.1 The instrument reproducibility was measured by analyzing five identical samples consisting of a 50/50 mixture of the cis- and trans- isomers and five identical samples of a 64/36 mixture of the cis- and trans- isomers.

7.2.3 The results indicate that the standard deviation for the instrument reproducibility is on the order of ±5% for the Hall Detector when the concentrations of the test solutions are the same.

7.2.3 Table of data used in the calculation of instrument reproducibility.

Table 7-2. Instrument Reproducibility Using the Hall Detector.

	Data Counts Cis-Telone			Data Counts Trans-Telone		
Solution ID	Set #1	Set #2	Set #3	Set #1	Set #2	Set #3
A	47,380			43,555		
B	50,652			42,644		
C	49,624	48,086	48,583	47,124	45,377	43,886
D	47,123	47,629		44,391	44,457	
E	52,331	52,680	55,252	45,946	46,199	49,724
Mean Value:	49,935 ± 2,731			45,334 ± 2,052		
Percent Variation:	5.4 %			4.5 %		
F	54,957			28,264		
G	58,339			29,245		
H	57,761	56,686	56,738	31,152	28,750	28,933
I	58,074	49,490	54,129	29,351	24,615	26,786
J	54,706	58,586	52,726	29,309	24,876	27,605
Mean Value:	55,659 ± 2,798			28,080 ± 1,983		
Percent Variation:	5.0 %			7.1 %		

Note: Solutions A, B, C, D, and E contain a nominal concentration of 4ng/ul of a 50/50 isomer mixture of 1,3-dichloropropene. Solutions F, G, H, I, and J contain a nominal concentration of 4.0 ng/ul of a 64/36 isomer mixture of 1,3-dichloropropene.

7.3 Determination of Instrument Reproducibility for multiple sample analysis

7.3.1 The instrument reproducibility was checked for multiple sample runs using the results of control sample analyses. The control samples were analyzed after every four analytical tests.

7.3.2 Table of data used in the determination of analytical reproducibilty.

Table 7-3. Data Used to Determine Analytical Reproducibility.

Sample Number	(Analysis of 4/19/90) Area Counts			(Analysis of 5/04/90) Area Counts		
	Cis-	Trans-	TCE	Cis-	Trans-	TCE
1	30493	27987	26080	64389	58073	39968
2	29418	28253	24825	63485	56714	38917
3	30586	27709	26271	58828	53187	36287
4	35531	32003	29946	57316	53060	36196
5	30734	27610	26317	59699	53466	35621
6	30388	26876	25962	54948	49068	32462
AVERAGE	31192	28406	26567	59778	53928	36575
STD DEV	2177	1822	1744	3614	3165	2648
% DEV	7.0%	6.4%	6.6%	6.0%	5.9%	7.2%

Note: The analyses of 4/19/90 and 5/04/90 are actual test sample data for analytical runs with normal operation. The percent variation of control samples will vary nominally from 5-15%.

7.4 Determination of the Average Calibration Curve

7.4.1 The variability of the instrument response and the detector-induced broadening of the GC peaks for the Hall Detector was treated by using a log-log fit to the calibration curve.

7.4.2 The day-to-day calibration/response curve was normalized to an arbitrary integration count at an analyte concentration of 2.0 ng/ul to account for trends in the day-to-day detector response.

7.4.3 An average calibration curve was derived for the area count response for both the cis- and trans-1,3-dichloropropene for comparison of the calibration curves on a daily basis. The parameters are defined in Table 7.4

7.4.4 Table of data used in the determinaion of the average calibration curve.

Table 7.4 Data used in the Determination of the Average Calibration Curve for the Hall Detector.

	Cis-1,3-dichloropropene			Trans-1,3-dichloropropene		
Date	Slope	Intercept	Count*	Slope	Intercept	Count*
4/13/90	1.1139	4.0564		1.1709	4.0036	
4/16/90	1.0830	4.0189		1.1912	3.9628	
4/17/90	1.0603	4.0907		1.1120	4.0167	
4/18/90	1.0148	4.1267		1.1046	4.0612	
4/19/90	1.0959	4.0581		1.1323	4.0230	
MEAN VALUE	1.0736	4.0702		1.1422	4.0115	
STD. DEV.	0.0342	0.0363		0.0376	0.0323	

* Area count at an analyte concentration of 2.0 ng/ul.

7.5 Significant factors affecting the reproducibility of the Hall detector.

7.5.1 Catalyst Renewal - The nickel catalyst can easily loose response if exposed to propanol or solvent extract (ethyl acetate or methanol). This is the first renewable part of the detector to be replaced when response is lost.

7.5.2 Detector solvent flow rate - The optimum solvent flow is in the range 0.4-1.0 cc/min. Higher solvent flows reduce sensitivity, and lower solvent flows increase peak tailing.

7.5.3 Detector contamination - Cleaning of the detector is recommended for optimum results. This factor appears to be the least significant for optimum detector performance.

APPENDIX IV.

Date: April 11, 1990

To: Don Fitzell, Engineering Evaluation Branch, MLD

From: Michael Poore, Northern Laboratory Branch, MLD

Subject: Confirmation of Presence of Telone (1,3-Dichloro-1-propene) in Carbon Disulfide Extracts

As requested, the staff has analyzed three extracts for telone, a pesticide consisting of a mixture of cis- and trans-1,3-dichloropropene isomers. The analysis was performed using a Finnigan OWA-20 GC/MS equipped with a splitless injection system and a 30 meter X 0.32 mm i.d. DB-Wax capillary column. The analytical system was calibrated using a 100 ug/ml (78 ug/ml cis, 21 ug/ml trans) telone standard in carbon disulfide. The mass spectra of the standard and the samples matched at a level of 0.99 with the computerized NBS spectral library. The results of the analyses are reported below.

SAMPLE	TELONE, ug/ml
2H	196
2R	238
2S	41

The chromatograms and mass spectral data are available on hardcopy and will be placed on file for 12 months. If you have any questions concerning these analyses, please feel free to contact me at 4-1970.

cc: WVL
DCC
RCK
GYL
LWB

APPENDIX V.

State of California
Air Resources Board

Quality Assurance Plan for Pesticide Monitoring

Prepared by the

Monitoring and Laboratory Division
and
Stationary Source Division

September 28, 1990

APPROVED:

Geroniave A. Shuma, Chief,
Toxic Air Contaminant
Identification Branch
Stationary Source Division

_____, Chief,
Quality Management and
Operations Support Branch
Monitoring and Laboratory Division

George Lew, Chief,
Engineering Evaluation Branch
Monitoring and Laboratory Division

This Quality Assurance Plan has been reviewed by the staff of the California Air Resources Board and approved for publication. Approval does not signify that the contents necessarily reflect the view and policies of the Air Resources Board, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

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QUALITY ASSURANCE PLAN FOR PESTICIDE MONITORING

I. Introduction

At the request of the Department of Food and Agriculture (DFA), the Air Resources Board (ARB) documents the "level of airborne emissions" of specified pesticides. Short-term (one month) ambient monitoring will be conducted in the area of, and during the season of, peak pesticide applications. In addition, monitoring of a field during and after application (up to 72 hours) will occur. The purpose of this document is to specify quality assurance activities for sampling and laboratory analysis of the pesticide.

II. Quality Assurance Policy Statement

It is the policy of the ARB to provide DFA with as reliable and accurate data as possible. The goal of this document is to identify procedures that ensure the implementation of this policy.

III. Quality Assurance Objectives

Quality assurance objectives for pesticide monitoring are: 1) to establish the necessary quality control activities relating to site selection, sample collection, sample analysis, and data validation, and 2) assessment of data quality in terms of precision, accuracy and completeness.

IV. Siting

Siting criteria for ambient pesticide monitoring are listed in TABLE 1. The monitoring objective for these sites is to measure population exposure near the perimeter of towns or in the area of the town where the highest concentrations are expected based on prevailing winds and proximity to applications. Background sites should be located away from any applications.

Siting criteria for placement of samplers near a pesticide application for collection of short-term samples are: 1) fifteen yards upwind of the field, 2) fifteen yards downwind of the field, and 3) 150 yards downwind of the field. These are only guidelines, since conditions at the site will dictate the placement of monitoring stations. Data on wind speed and direction will be collected during application monitoring. Once monitoring has begun, the sampling stations will not be moved, even if the wind direction has changed. Field application monitoring will follow the schedule outlined in TABLE 2. This schedule and study design are consistent with requests from DFA for monitoring near a pesticide application.

A. Monitoring Site Description

The protocol for ambient monitoring should include a map of the monitored area which shows nearby towns or communities and their relationship to the monitoring stations. A site description should be completed for any monitoring site which might have characteristics that could affect the monitoring results (e.g., obstructions).

Similarly, a map or sketch of the monitoring stations should be made with respect to the application field.

V. Sampling

Samples for ambient pesticide monitoring will be collected over 24-hour periods on a schedule, in general, of 4 samples per week for 4 weeks. Sampling will be conducted following the Environmental Protection Agency (EPA) ambient monitoring guidelines of 40 CFR 58 for calibration, precision, accuracy and data validation. The ARB Quality Assurance Section upon request will review quality assurance/quality control procedures and will evaluate pesticide monitoring activities.

A. Protocol

Prior to conducting any pesticide monitoring a protocol will be written that describes the overall monitoring program and includes the following topics:

1. Identification of the sample site locations.

2. Description of the sampling train and a schematic showing the component parts and their relationship to one another in the assembled train, including specifics of the sampling media (e.g., resin type and volume, filter composition, pore size and diameter, catalog number, etc.)

3. Description of the analytical method.

4. Quality assurance/quality control plan for sampling, including calibration procedures for flow meters.

5. Test schedule.

6. Test personnel.

Specific sampling methods and activities will be described in a monitoring plan (protocol) for review by ARB and DFA. Criteria which apply to all sampling are: 1) chain of custody forms will accompany all samples (APPENDIX I.), 2) light and rain shielding will be used for samples during monitoring and, 3) samples will be stored in an ice chest until delivery to the laboratory. The protocol should include: equipment specifications (when necessary), special sample handling and an outline of sampling procedures. The protocol should specify any procedures unique to this specific pesticide.

B. Log Sheets

Field data sheets will be used to record sampling date and location, initials of individuals conducting sampling, sample type (e.g., charcoal tube), sample number or identification, initial and final time, initial and final flow rate, malfunctions, leak checks, weather conditions (e.g., rain) and any other pertinent data which could influence sample results. Field blanks should be included with each batch of samples submitted to the lab for analysis. The average of the initial and final flow rates for the sampling period will be used if a flow controller is not used.

C. Collocation

For ambient monitoring, sampling precision or the standard deviation of the data set will be calculated from at least 2 samples collocated at a site. The collocated sampler will be rotated between sampling sites so that at least three duplicate samples are collected at each site. The samplers should be located between two and four meters apart if they are high volume samplers in order to preclude airflow interference. This consideration is not necessary for low (<20 liters/min.) flow samplers. One sample will be designated as the primary sample and the other sample will be designated as the duplicate.

D. Calibration

If elapsed time meters are used, rather than noting beginning and ending times, the meters should be checked and calibrated to within $\pm$ 5 minutes for a 24-hour period. Samplers operated with an automatic on/off timer should be calibrated so that the sampling period is 24 hours $\pm$ 15 minutes.

Flow meters, flow controllers or critical orifices should be calibrated against a referenced flow meter prior to a monitoring period.

Sampling flows should be checked in the field and noted before and after each sampling period. Before flows are checked, the sampling system should be leak checked. The initial flow should be within $\pm$ 10% if a calibrated pressure transducer is used to check the flows, or within $\pm$ 15% if a calibrated rotameter is used. Flow meters should be recalibrated if flows are found to be outside of those control limits.

E. Preventative Maintenance

To prevent loss of data, spare pumps and other sampling materials should be kept available in the field by the operator. A periodic check of sampling pumps, meteorological instruments, extension cords, etc. should be made by sampling personnel.

TABLE 1. PESTICIDE MONITOR SITING CRITERIA SUMMARY

The following probe siting criteria apply to pesticide monitoring and are summarized from the EPA ambient monitoring criteria (40 CFR 58) which are used by the ARB.

Height Above Ground (Meters)	Minimum Distance From Supporting Structure (Meters)		Other Spacing Criteria
	Vertical	Horizontal	
2-15	1	1	1. Should be 20 meters from trees. 2. Distance from sampler to obstacle, such as buildings, must be at least twice the height the obstacle protrudes above the sampler. 3. Must have unrestricted air-flow 270° around sampler. 4. Samplers at a collocated site (duplicate for quality assurance) should be 2-4 meters apart if samplers are high flow, >20 liters per minute.

TABLE 2. APPLICATION SAMPLING SCHEDULE

The sampling schedule for each station is as follows:

	Samples per Site*		
	~15 yds up-wind	~15 yds down-wind	~150 yds down-wind
- Background sample (1 hr. sample: prior to application).	2	2	2
- Application + 1 hr. after application combined sample.	2	2	2
- 2 hr. sample from 1 to 3 hours after the application.	2	2	2
- 4 hr. sample from 3 to 7 hours after the application.	2	2	2
- 8 + hr. sample from 7 to 15+ hours after the application.	2	2	2
- 9 + hr. sample from 15 to 24+ hours after the application.	2	2	2
- 1st 24 hour sample starting at the end of the 9+ hr. sample.	2	2	-
- 2nd 24 hour sample starting 24 hrs after the end of the 9+ hr. sample.	2	2	-

* duplicate collocated samples at each site.

VI. Analysis

Analytical audits should be conducted by spiking the sample medium with the reference standard. These can then be carried into the field and handled as actual samples (trip spike) or run at the background site for ambient monitoring (field spike) prior to delivery to the laboratory for analysis. At least one spike per monitoring period is required and one spike per week is recommended for ambient monitoring.

Analysis methods should be documented in a Standard Operating Procedure (S.O.P.) before monitoring begins. The S.O.P. should include: instrument and operating parameters, sample preparation, calibration procedures and quality assurance procedures.

A. Standard Operating Procedures

1. Instrument and Operating Parameters

A complete description of the instrument and the conditions should be given so that any qualified person could duplicate the analysis.

2. Sample Preparation

Detailed information should be given for sample preparation including equipment and solvents required.

3. Calibration Procedures

The monitoring plan will specify calibration procedures including intervals for recalibration, calibration standards, environmental conditions for calibrations and a calibration record keeping system. When possible, National Institute of Standards and Technology traceable gas standards should be used for calibration of the analytical instruments in accordance with standard analytical procedures which include multiple calibration points that bracket the expected concentrations.

4. Quality Assurance

Validation testing should provide an assessment of accuracy, precision, interferences, method recovery, analysis of pertinent breakdown products and limits of detection. Method documentation should include confirmation testing with another method when possible, and quality control activities necessary to routinely monitor data quality control such as; use of control samples, control charts, use of surrogates to verify individual sample recovery, field blanks, lab blanks and duplicate analysis. All data should be properly recorded in a laboratory notebook.

The method should include the frequency of analysis for quality control samples. Analysis of quality control samples are

recommended before each day of lab analysis and after every tenth sample. Control samples should be found to be within control limits previously established by the lab performing the analysis. If results are outside the control limits, the method should be reviewed, the instrument recalibrated and the control sample reanalyzed.

All quality control studies should be completed prior to sampling and include recovery data from at least three samples spiked at at least two concentrations. Instrument variability should be assessed with three replicate injections of a single sample at each of the spiked concentrations. A stability study should be done with triplicate spiked samples being stored under actual conditions and analyzed at appropriate time intervals. Prior to each sampling study, a conversion/collection efficiency study should be conducted under field conditions (drawing ambient air through spiked tubes at actual flow rates for the recommended sampling time) with three replicates at two spiked concentrations and a blank. Breakthrough studies should also be conducted to determine the capacity of the adsorbent material if high levels of pesticide are expected or if the suitability of the adsorbent is uncertain.

VII. Data Reduction and Reporting

The mass of pesticide (microgram, ug) found in each sample will be used along with the sample air volume from the field data sheet to calculate the mass per volume for each sample. For each sampling date and site, concentrations should be reported in ug/m^3 as well as ppb or ppt (as appropriate). Wind speed and direction data will also be reported for application site monitoring.

Ambient data should be summarized for each monitoring location by maximum and second maximum concentration, average (using only those values greater than the minimum detection limit), total number of samples and number of samples above the minimum detection limit. For this purpose, collocated samples are averaged and treated as a single sample.

A. Quality Assurance

Quality assurance activities and data will be summarized by the staff conducting the sampling and included as an attachment to the final data summary. The quality assurance report will include a summary of the average data precision, accuracy, and completeness.

1. Precision and Accuracy

   The average precision or standard deviation will be reported based on the comparison of the collocated sampling data. Accuracy data to be reported includes the results of the analyses of spiked samples and the results of any flow audits.

2. Data Completeness

   Data completeness should be calculated as a percentage of valid data compared to the total possible amount of data if no invalidations had occurred. Data will be invalidated if the power is out at a site and the length of a sample time cannot be verified, or if any of the sampling medium is lost during sampling, shipment or analysis.

CALIFORNIA AIR RESOURCES BOARD
MONITORING & LABORATORY DIVISION
P.O. Box 2815, Sacramento CA 95812

CHAIN OF CUSTODY

SAMPLE RECORD

Job #: _____ Date: _____
Sample/Run #: _____ Time: _____
Plant name: _____
Sample Location: _____
Type of Sample: _____
Log #: _____ Initials: _____

ACTION	DATE	TIME	GIVEN BY	TAKEN BY
Sample Collected				
Transfer				
Transfer				
Transfer				
Transfer for Analysis				

Disposition of Sample: Immediate Analysis ____ Refrigerator ____
Storage ____ Freezer ____

RELATED ID'S	DESCRIPTION

RETURN THIS FORM TO: Don Fitzell (445-0618)

APPENDIX VI.

State of California

M E M O R A N D U M

To : George Lew, Chief
Engineering Evaluation Branch
Monitoring and Laboratory Division

Date : November 6, 1990

Subject : Telone Audit Report

Alice Westerinen, Manager
Quality Assurance Section
Monitoring and Laboratory Division
From : Air Resources Board

Please find attached the Quality Assurance Audit Report on the Telone Monitoring Project in Merced County. The report consists of three parts: the results of a field audit conducted on April 18, 1990, at the five monitoring sites in Merced County, and the results of two system and analytical audits conducted on April 25 through April 27, 1990, for the Engineering Evaluation Branch, and July 12 through August 10, 1990, for the Southern Laboratory Branch.

If you have any questions regarding the report, please contact me at (916) 324-6191.

Attachment

cc: Don Crowe
Jim Shikiya

November 6, 1990

Audit Report
Telone Monitoring in Merced County

SUMMARY

Field Audit

On Wednesday, April 18, 1990, Quality Assurance (QA) staff of the California Air Resources Board (ARB) conducted a field audit of the Telone Air Monitoring Project by the ARB's Engineering Evaluation Branch (EEB). Performing the audit was Fred Burriell of the QA staff. Lyle (Bud) Thoma was the field operator for the EEB.

The field audit consisted of verifying whether the siting of the monitoring stations conformed with the Stationary Source Division (SSD) 1986 draft of the "Quality Assurance Plan For Pesticide Monitoring" and the Code of Federal Regulations (CFR) 40, Part 58, Appendix E, July 1, 1988 Edition. The audit included a visual inspection of the maintenance records, a review of site activity documentation and an evaluation of the handling and shipping procedures. The flow of each sampling apparatus was audited with a National Institute of Standards and Technology (NIST) traceable Matheson 10 lpm Mass Flow Meter (MFM). All of the five monitoring sites which were in operation for the project were audited.

Two siting deficiencies were observed. First, at the site located in El Nido, the inlet probe was located within 5 meters of a tree dripline. Second, at the Dos Palos Y site, a "rover" sampler was collocated within one foot of the site sampler. Although there is no regulation governing proximity, Carol Bohnenkamp of the Environmental Protection Agency (EPA), advises that the Lo-Vol samplers meet the same requirements as the Hi-Vol samplers, which require collocated samplers to be placed at least two (2) meters apart. No other deviations from the established siting criteria were noticed; however, it was observed that maintenance workers were applying a tar substance containing petroleum distillates to a roof within 15 feet of the intake probe at the Merced County Hospital site.

With two exceptions, documentation for field operations recording site maintenance and sample collection information were consistent with good practice. These two exceptions consisted of a lack of calibration data for the Dwyer rotameters used to set the sample flows and the lack of a Field Standard Operating Procedure (SOP). However, flow audits of the Telone samplers demonstrated that the sampler flows, as measured by the Dwyer rotameters, were all within 5% of the flows measured by the NIST traceable audit device. A slight negative bias was observed in the flow audit results averaging -2.7% with a range of -4.7% to +0.2%. This indicates that the original calibration using a mercury manometer to measure pressure drop and a double check of two of the samplers utilizing a bubble meter was sufficient to produce good flow results.

System Audit

A laboratory system audit was conducted on April 25 through April 27, 1990, at the Monitoring and Laboratory Division (MLD) - Engineering Evaluation Branch (EEB) laboratory, which was providing analytical support for the Telone Monitoring Project. Another audit was conducted on July 12 through August 10, 1990, at the Southern Laboratory Branch (SLB), which performed confirmation analyses during the project. Don Fitzell represented the EEB laboratory and Leo Zafonte represented the SLB during the audit, which was conducted by Gabriel Ruiz of the Quality Assurance Section.

The laboratory audit was composed of both a system and an analytical performance audit. The system audit consisted of a review of laboratory instrumentation used for the Telone project and the quality control measures pertaining to sample handling, analysis and documentation. For the analytical performance audit, charcoal adsorbant tubes were spiked with Telone by QA staff and submitted to the laboratory for analysis.

The results of the EEB audit show that good quality control practices were observed in the areas of sample handling and storage, sample analysis, sample documentation, and method validation and confirmation. Deficiencies were noticed in the areas of instrumentation log books and performance assessment, and improvements on data validation would be made if the laboratory routinely analyzed field and laboratory spiked samples.

The EEB laboratory's reported audit results were all within 32% of the assigned values. The percent difference averaged 11.1% and ranged from 0.0% to 31.2%. The results of confirmation analyses by MLD's Northern Laboratory Branch showed an average percent difference of 7.4% with a range of -12.0% to +51.2%.

Good quality control practices were also followed by the Southern Laboratory Branch. The only deficiencies noted were the lack of a written SOP before any analyses were conducted, the exclusion of laboratory spikes and the lack of instrument log books. The results of the analytical performance audit showed a positive bias ranging from +4.8% to +24.0% and averaging 15.8%.

FIELD AUDIT

Sampler Siting

The five monitoring sites were located at the Merced County Hospital in Merced, the Merced County Fire Department in El Nido, the Merced County Fire Department in Dos Palos, the Merquin School in Stevinson, and the Hilmar Junior High School in Hilmar. Each site was evaluated on Wednesday, April 18, 1990, by QA staff for conformance with the siting criteria outlined in the Stationary Source Division (SSD) 1986 draft of the "Quality Assurance Plan For Pesticide Monitoring" and the CFR 40, Pt. 58, App. E (7-1-88 edition). These criteria for siting the samplers are listed in Table I, along with the summary of the audit findings. If no "X" appears in the space provided, the sampler did not meet the criteria and the deficiency is explained in the table notes.

At all sites, the design was such that the sampler inlet probe was not located at least 1 meter horizontally from the supporting rod. However, the design of the support rod was such that the sampler had a greater than 270 degree unrestricted airflow around the probe inlet, and it is our belief that this deficiency had no significant impact on sample integrity. At the El Nido site a tree dripline was within 5 meters of the probe inlet, and the samplers at the Dos Palos site did not meet the criteria for collocated samplers, as they were significantly less than 2 meters apart. No other deviations from the established siting criteria were noticed; however, it was observed that maintenance workers were applying a tar substance containing petroleum distillates to a roof within 15 feet of the inlet probe at the Merced County Hospital site.

Table I. Pesticide sampler conformance with siting criteria.

SITE LOCATION	Height from Ground 2-15 meters	Distance from Supporting Structure		Should be 20 meters from tree dripline	Distance from obstacles must be two times the height the obstacle protrudes above the sampler	Unrestricted airflow, 270 degrees around the sampler	No furnace or incineration flues within 10 meters
		Vertical 1 meter	Horizontal 1 meter				
Merced Merced County Hospital 210 East 15th Street Merced, CA.	X	X	1	X	X	X	X
El Nido Merced County Fire Department 10537 S. Hwy 59 at El Nido Rd. El Nido, CA.	X	X	1	2	X	X	X
Dos Palos Y Merced County Fire Department 8047 Dairy Lane Dos Palos, CA.	X	X	1	X	3	X	X
Dos Palos Y Merced County Fire Department 8047 Dairy Lane El Nido, CA.	X (R)	X	1	X	3	X	X
Stevinson Merquin School 3rd Ave. west of Highway 165 Stevinson, CA.	X	X	1	X	X	X	X
Hilmar Hilmar Jr. High School Lander Ave. north of Geer Ave. Hilmar, CA.	X	X	1	X	X	X	X

Table Notes:

1 = The sample inlet probe was placed less than 1 meter horizontally from the pole used to support the sample line and absorbant tube.
2 = A tree dripline was located within 5 meters of the inlet probe.
3 = Collocated samplers were located less than 2 meters apart. Although this is a requirement for Hi-Vol samplers, it is not required of, but advised for the Lo-Vol samplers as well.

R = Rover sampler which is moved from site to site on a weekly basis.

Field Operations

The sampler apparatus was designed by the Monitoring and Laboratory Division (MLD) Engineering Evaluation Branch (EEB) staff. The sampler consisted of a stainless steel inlet probe connected to two charcoal adsorption tubes. All of the samplers used nylon connectors between the sample inlet and the adsorption tubes. The tubes were vertically mounted and covered with aluminum foil to protect them from sunlight. Each tube was connected with latex tubing to a Dwyer rotameter placed in line to measure the flows. The rotameters were adjusted to obtain a 3 lpm flow rate. The rotameters were then connected with latex tubing to a single Thomas pump (see Figure 1).

Duplicate samples were collected for 24-hour periods. After each sampling period, the samples were removed, capped, labeled and stored inside individual screw-cap glass culture tubes in an ice chest until delivered to the laboratory. On Friday of each week, half of the samples were delivered to the Engineering Evaluation Branch laboratory in Sacramento, and the other half were transported by plane to Burbank and delivered to the Southern Laboratory Branch in El Monte for confirmation analysis. All samples were accompanied by a field data sheet for each day of sampling and chain-of-custody forms.

Field blanks were submitted to the laboratories on a weekly basis. Duplicate field spikes were prepared by Don Fitzell of the Engineering Evaluation Branch, to be analyzed by EEB and by SLB.

A Field Standard Operating Procedure was not available prior to the beginning of monitoring. Records were up to date and adequate for the study. The information recorded on field data sheets by the technician included sample start and stop times, measured flow, sample volume, field operator, date, sampler location, comments as to unusual field conditions, and maintenance performed.

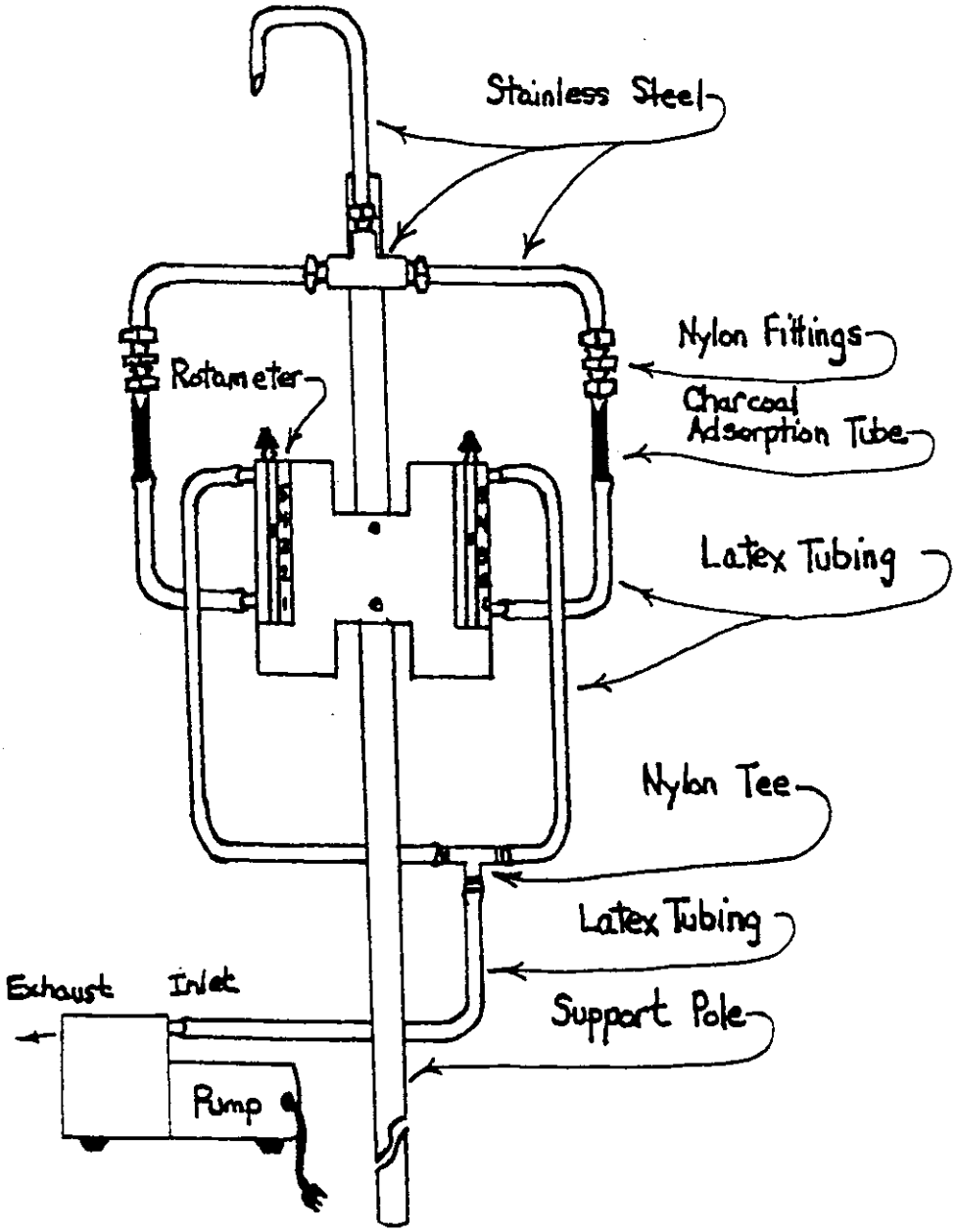

Figure 1. Telone Sampler

Field Flow Audits

Flow accuracy measurement audits were conducted with an NIST traceable 10 lpm Matheson Mass Flow Meter, Model 8148, Serial Number BC103049 and performed according to the procedures outlined in Attachment I. The mass flow meter was certified against a primary standard Brooks Automatic Flow Rate Calibrator, Model 1050. Results of the "As Found" flow audits are summarized in Table II. A small negative bias, averaging -2.7%, was observed in the audit results, which indicates the flow checks of the Dwyer rotameters were performed correctly. An additional flow audit was performed after the adsorption tubes were changed and the flows reset by the field operator. The results of the flow audit are contained in Table III.

Table II. "As Found" flow accuracy audit results.

Site	Sampler ** Flow, L/min.	True Flow, L/min.	Percent Difference*
Merced Co. Hospital	6.0	5.81	-3.3
El Nido Fire Dept.	6.0	5.96	-0.7
Dos Palos Fire Dept. "Rover"	6.0	6.01	+0.2
Dos Palos Fire Dept.	6.0	5.73	-4.7
Stevinson Merquin School	6.0	5.73	-4.7
Hilmar Jr. High School	6.0	5.83	-2.9

* Percent Difference = $\frac{\text{True Flow - Sampler Flow}}{\text{True Flow}} \times 100$

** Single inlet probe supplying 2 tubes and 2 rotameters.

Table III. Flow accuracy audit results after replacement of the adsorption tubes.

Site	Sampler ** Flow, L/min.	True Flow, L/min.	Percent Difference*
Merced Co. Hospital	6.0	5.86	-2.4
El Nido Fire Dept.	6.0	5.99	-0.2
Dos Palos Fire Dept. "Rover"	6.0	6.15	+2.4
Dos Palos Fire Dept.	6.0	5.98	-0.3
Stevinson Merquin School	6.0	5.97	-0.5
Hilmar Jr. High School	6.0	5.84	-2.7

* Percent Difference = $\frac{\text{True Flow - Sampler Flow}}{\text{True Flow}} \times 100$

** Single inlet probe supplying 2 tubes and 2 rotameters.

Post-Study Flow Audits

On Tuesday, May 15, 1990, Quality Assurance (QA) staff conducted post-study flow audits of the five (5) site samplers and one (1) rover sampler used to conduct the Telone Monitoring Project. The post-study flow audits were conducted in the same manner as the field flow audits with one exception: the audits were performed while the samplers were in the Engineering Evaluation Branch shop located at 15th and R Streets in Sacramento, California. The audits were performed by Fred Burriell.

Table IV contains the results of the post-study flow audits in the "As Found" condition, while Table V contains the results of the post-study flow audits after replacement of the charcoal adsorption tubes. To present the data in proper perspective, the samplers were audited in the same order as they were in the field and are thus listed under those site names to properly identify each sampler.

Table IV. Post-Study "As Found" flow accuracy audit results.

Site	Sampler ** Flow, L/min.	True Flow, L/min.	Percent Difference*
Merced Co. Hospital	6.0	5.90	-1.7
El Nido Fire Dept.	6.0	6.05	+0.8
Dos Palos Fire Dept. "Rover"	6.0	6.07	+1.2
Dos Palos Fire Dept.	6.0	5.91	-1.5
Stevinson Merquin School	6.0	5.95	-0.8
Hilmar Jr. High School	6.0	5.84	-2.7

* Percent Difference = $\frac{\text{True Flow} - \text{Sampler Flow}}{\text{True Flow}} \times 100$

** Single inlet probe supplying 2 tubes and 2 rotameters.

Table V. Post-Study flow accuracy audit results after replacement of the adsorption tubes.

Site	Sampler ** Flow, L/min.	True Flow, L/min.	Percent Difference*
Merced Co. Hospital	6.0	5.90	-1.7
El Nido Fire Dept.	6.0	6.06	+1.0
Dos Palos Fire Dept. "Rover"	6.0	6.03	+0.5
Dos Palos Fire Dept.	6.0	5.94	-1.0
Stevinson Merquin School	6.0	5.94	-1.0
Hilmar Jr. High School	6.0	5.96	-0.7

* Percent Difference = $\frac{\text{True Flow} - \text{Sampler Flow}}{\text{True Flow}} \times 100$

** Single inlet probe supplying 2 tubes and 2 rotameters.

The post-study flow audit results in the "As Found" condition indicate that the samplers were all within ±3% of the Standard Flow Rate, with a range of -2.7 to +1.2%. A small negative bias is observed in the post audit results, the average being -0.8%.

The post-study flow audit results, after the adsorption tubes were changed, also indicated a small negative bias of -0.5%. All samplers were within ±2% of the Standard Flow Rate, with a range of -1.7 to +1.0%.

The repeatability of these results indicate a sufficient method for calibrating and flow checking the samplers under both field and laboratory conditions.

ENGINEERING EVALUATION BRANCH SYSTEM AUDIT

A system audit of the Engineering Evaluation Branch laboratory operations was conducted on April 25 through April 27, 1990. The audit consisted of a review of the instrumentation, a review of the quality control measures used to monitor data quality, and an analytical performance audit. The following is a discussion of the audit findings.

Laboratory Instrumentation

The instrumentation used for the analysis of the Telone samples was a Varian 3400 Gas Chromatograph equipped with an Electron Capture Detector (GC/ECD) interfaced to a Varian 604 Data System.

Sample Handling and Storage

The samples were delivered to the laboratory on Friday of each week, accompanied by a field record sheet for each day of sampling and chain-of-custody forms. The samples were stored in a refrigerator at 4°C until analyzed. Sample extraction and analysis were performed within one week.

To verify the integrity of Telone samples under normal storage conditions, stability studies were done for triplicate sets of 1.0 ug spikes. Analysis of the samples at 1, 3, 5, 11 and 38 days resulted in recoveries of 95%, 77%, 77%, 81% and 68%, respectively. During the study, no sample migration from the primary section to the secondary section of the tube was observed.

Sample Analysis

The analytical procedure was adapted from NIOSH Method 1003 (issued 2/14/84), and was documented in a preliminary draft entitled "Standard Operating Procedure for the Analysis of 1,3-dichloropropene (Telone) in Ambient Air". Briefly, the method entails extraction of the exposed charcoal tube with carbon disulfide and analysis of the extract by gas chromatography. Refer to the SOP draft for further details of the method.

The method was validated for the following parameters: detection limit (0.4 ug/tube) (3X Std. Dev. at lowest calibration point plus the absolute value of the intercept), method recovery (>90%), instrument linearity in the 0.05 to 10 ug range, and sample stability under normal storage conditions. Initially, sample breakthrough studies were performed only for a total mass up to 40 ug of Telone per tube; however, analysis of the secondary section of field samples containing up to 760 ug/tube revealed no sample breakthrough.

Quality control activities performed on a routine basis to monitor and document the laboratory data quality included a daily three point instrument calibration, weekly field blanks, field duplicates from collocated samplers (4/week), and a one time field spike. In addition, a number of the samples analyzed were confirmed by Mass Spectroscopy (GC/MS) by MLD's Northern Laboratory Branch.

A duplicate set of samples was sent weekly to MLD's Southern Laboratory Branch for independent analysis by Gas Chromatography with a halogen-specific Hall Detector.

Documentation

Each sample was given a unique sample number in the field, and the same number was used in the laboratory. A chain-of-custody documentation system was established, and records were kept for each sample batch. Field and laboratory data sheets, and chain-of-custody records were maintained in an accessible form by the laboratory staff.

A bound notebook with numbered pages was kept in the laboratory, and all sample analysis entries were made in ink. The entries included sample identification number, a file number, date of analysis, raw analytical data, and results of the analysis.

Analytical Performance Audit

The performance of the analytical method was evaluated by submitting for analysis a set of samples prepared following the procedure outlined in Attachment II. A duplicate sample set was submitted to MLD's Northern Laboratory Branch for confirmation. Results of the performance audit are summarized in Table VI.

The Engineering Evaluation Branch audit results showed a positive bias ranging from 0.0% to +31.2% and averaging +11.1%. Most of the results were within 11.2% of the assigned value, and duplicate samples agreed very closely with each other. The Northern Laboratory Branch results had an average percent difference of +7.4% with a range of -12.0% to +51.2%.

Table VI. Results of the Engineering Evaluation Branch analytical performance audit and confirmation results by the Northern Laboratory Branch.

		ENGINEERING EVALUATION BRANCH		NORTHERN LABORATORY BRANCH	
Sample ID	Assigned Mass (ug)	Reported Mass (ug)	Percent Difference	Reported Mass (ug)	Percent Difference
A1	5.0	5.0	0.0 %	4.6	-8.0 %
A2	100.0	131.2	+31.2	99.2	-0.8
A3	25.0	27.3	+9.2	37.8	+51.2
A4	0.0	<0.1*	---	<1*	---
A5	5.0	5.2	+4.0	5.4	+7.2
A6	25.0	27.8	+11.2	22.0	-12.0

* Below Limit of Detection

$$\text{Percent Difference} = \frac{\text{Reported Mass} - \text{Assigned Mass}}{\text{Assigned Mass}} \times 100$$

Recommendations

The results of the system audit show that good quality control practices were followed in the areas of sample handling and storage, sample analysis, sample documentation, and method validation and confirmation. Deficiencies were noticed in the areas of instrumentation log books and performance assessment. Although the deficiencies were not significant enough to compromise the overall data quality, the Quality Assurance Section recommends taking the following steps to reinforce the validity of the results:

1. Field and Laboratory Spikes

   Whenever possible, field spikes should be included with the weekly batch of samples submitted to the laboratory to allow the determination of any errors introduced during sample transport and to document sample recoveries. Also, laboratory spikes should be routinely analyzed to monitor sample recovery.

2. Response Factor Plots

A record of the response factor (the ratio of concentration to the instrument area count) should be kept for at least one of the calibration standards. A plot of the daily response factors would allow the analyst to monitor the instrument sensitivity over time, so that changes in the operating parameters, such as column or detector degradation, or degradation of the standards, can be detected.

3. Instrument Maintenance Log

A maintenance log book should be kept for the gas chromatograph. A record of all services performed should be kept as it may be important in determining the cause of a change in instrument performance.

ENGINEERING EVALUATION BRANCH SYSTEM AUDIT FOLLOW-UP

Shortly after the system audit was completed, the EEB laboratory staff discovered that the manufacturer of the column (J & W Scientific) indicated a trans- then cis- elution order in their 1989-90 catalog of "High Resolution Chromatographic Products", whereas the 1990-91 catalog indicated the reverse order. The EEB staff contacted the manufacturer and determined that the latter order was correct. Since the lab had used the elution order indicated in the 1989-90 catalog, the standard curves and analytical results had to be recalculated.

The revision resulted in only a slight increase for most of the data, because the relative abundance of the cis- and trans- isomers in the field samples was about the same. The revised audit results, however, exhibited a considerable increase, because the isomers were present in a 78% to 22% cis- to trans- ratio. The average percent difference changed from -16.3% to +33.5%.

The EEB staff was asked to account for the large change in the audit results. It was found that the measured ratio of the cis- to trans- isomers in the standard used for calibrations did not agree with the ratio assigned by the manufacturer (Supelco). The laboratory results indicated a 60% to 40% ratio, while the manufacturer indicated a 76% to 24% ratio. An effort was made to clear this discrepancy, but the manufacturer was unable to verify the correct ratio. Since the issue could not be resolved, it was decided that instead of quantifying the individual cis- and trans- peaks and then adding them to obtain total Telone, as had been done throughout the study, the individual peaks would be first added, and the total Telone would be calculated from the combined area counts. The standard curves and analytical results were recalculated for a second time, and the results were reported as the total of the combined peaks. The average percent difference of the revised audit results decreased from a previous value of +33.5% to +11.1%, as reported in Table VI.

SOUTHERN LABORATORY BRANCH SYSTEM AUDIT

A system audit of the Southern Laboratory Branch operations in support of the Telone Monitoring Project was conducted on July 12 through August 10, 1990. The audit was conducted primarily through electronic mail and telephone conversations, and it consisted of a review of the instrumentation, a review of the quality control measures used to monitor data quality, and an analytical performance audit. The following is a discussion of the audit findings.

Laboratory Instrumentation

Analysis of the Telone samples was performed with a Varian 6000 Gas Chromatograph with a halogen-specific Hall Detector. The chromatograph was interfaced to a Varian Vista 402 Integrator. The integrator was used for area counts only, and the concentrations were determined by separate calculation.

Sample Handling and Storage

Samples were delivered to the laboratory accompanied by field data sheets and chain-of-custody records on Friday of each week. Receipt of the samples was recorded on the field data sheets and chain-of-custody forms, and the samples were stored in a freezer below 0^{0}C until extracted. Sample extraction and analysis were performed within one to three weeks, and the dates were recorded on the field data sheets. A copy of the data sheets was then attached to the laboratory book as a permanent record.

Sample Analysis

The analytical procedure was developed by laboratory staff. The method entails extraction with ethyl acetate/methanol followed by GC analysis with a DB-1 column and a halogen-specific Hall Detector. A Standard Operating Procedure for the method was not written before the analyses were made.

Quality control activities performed routinely to monitor and document the data quality included the following: daily calibration at five to seven points over the 1 to 100 ug/ml range, analysis of one control sample every four samples, plotting of control charts with control limits defined at $\pm$10%, a solvent blank per analytical sequence, and field duplicates from collocated samplers. In addition, analysis of some samples showing a positive response was repeated, and one field spike was analyzed.

The detection limit of the method was determined as 0.2 ug/ml using three Standard Deviations at lowest calibration point plus the absolute value of the intercept. Since the Hall Detector had a non-linear calibration curve over the 1 to 100 ug/ml range, a log-log linear fit of area count vs. concentration normalized at 2 ng/ul was used to determine the concentrations.

Documentation

The laboratory staff followed the chain-of-custody procedures established by the Engineering Evaluation Branch. All samples received were assigned a unique laboratory sample number which incorporated the field sample number.

A bound notebook with numbered pages was kept in the laboratory. The entries included sample number, sample type, date sample was received, date of analysis, raw analytical data, results of the analysis, and receptor of the analytical data. In addition, copies of field data sheets with collection and extraction data were attached to the laboratory book.

The chromatograms, integrator printouts, and summary sheets for the analysis sequence were saved in an accessible form. Raw data for most runs was stored on electronic media.

Analytical Performance Audit

The performance of the Southern Laboratory Branch (SLB) analytical method was evaluated by submitting for analysis a set of four spiked samples and a blank. The samples were prepared following the procedures outlined in Attachment II, with the exception that only the 1.0 mg/ml standard was used and the samples were spiked at 5 ug and 50 ug per tube.

The samples were extracted with 100% ethyl acetate and analyzed on August 3, 6 and 9. The averages of the results showed a positive bias ranging from +4.8 to +24.0% and averaging +15.8%. The audit results are summarized in Table VII.

Table VII. Results of the Southern Laboratory Branch analytical performance audit.

Sample ID	Assigned Mass (ug)	Reported Mass (ug)	Percent Difference
S1	0.0	0.0*	---
S2	50.0	52.4	+ 4.8%
S3	5.0	6.2	+24.0
S4	50.0	56.1	+12.2
S5	5.0	6.1	+22.0

* Below Limit of Detection

$$\text{Percent Difference} = \frac{\text{Reported Mass} - \text{Assigned Mass}}{\text{Assigned Mass}} \times 100$$

Recommendations

The results of the system audit show that good quality control practices were followed by SLB during the Telone Monitoring Project. The only deficiencies noted were that the SOP was not written before the analyses were performed, lab spikes were not analyzed, and an instrument log was not kept for the gas chromatograph. The Quality Assurance Section makes the following recommendations:

1. SOP

   The method should have a written SOP before any analyses for record are conducted. The SOP should be followed routinely, and deviations should be noted in the lab workbook.

2. Laboratory Spikes

   Laboratory spikes should be routinely analyzed to determine matrix effects and to monitor sample recovery.

3. Instrument Maintenance Log

A maintenance log book should be kept for the gas chromatograph. All services and repairs should be recorded in the log book as it may be important in determining the cause of a change in instrument performance.

ATTACHMENT I

Flow Audit Procedure for Pesticide Samplers

Introduction

The pesticide sampler is audited using a Matheson Mass Flow Meter, Model 8148, that is standardized against a NIST traceable Brooks Automatic Flow Calibrator, Model 1050, corrected to 25°C and 760 mm Hg.

The Mass Flow Meter (MFM) is placed in series with the sample probe inlet and the flows checked while the sampler is operating at the normal sampling flow rate. The standard (true) flow rates are obtained from the calibration curve of the MFM and the indicated flow rates are applied to the sampler's calibration curve to determine the reported flow rates which are then compared to the true flow rates. From this comparison, an actual percent difference is then determined.

Equipment

The basic equipment required for the pesticide sampler flow audit is listed below. Additional equipment may be required depending on the particular configuration and type of sampler.

1. Matheson Mass Flow Meter, Model 8148, Transfer Standard with a 10 SLPM transducer.
2. Teflon tubing, 1/4" I.D.
3. Plastic caps to cover flow meter ports.
4. 1/4" I.D. Tygon tubing to connect the Matheson 10 SLPM Mass Flow Meter to the sampler probe inlet.
5. Audit data sheets.

Audit Procedures

1. Plug the Matheson Mass Flow Meter into a 110 VAC outlet. Allow at least 10 minutes for the MFM to warm up.
2. Connect the Matheson MFM to the sampler probe inlet with the 1/4" teflon tubing and 1/4" I.D. Tygon tubing.
3. Allow the flow to stabilize for at least 1 - 2 minutes and record the indicated flows on the data sheet.

4. Apply the indicated flows to the calibration curve of the Matheson MFM standard to obtain the true flow and record the results in the blanks provided on the field data sheet. Obtain the sampler measured flow from the field operator. Calculate the difference between the true flow and the measured flow and report as percent difference on the field data sheet.

ATTACHMENT II

Performance Audit Procedure For The Laboratory Analysis Of Telone

Introduction

The purpose of the laboratory performance audit is to assess the accuracy of the analytical methods used by the laboratories measuring the ambient concentrations of Telone, a cis- and trans-1,3-dichloropropene mixture. The audit is conducted by submitting audit samples prepared by spiking charcoal tubes with known concentrations of 1,3-dichloropropene. The analytical laboratories report the results to the Quality Assurance Section, and the difference between the reported and the assigned concentrations is used as an indicator of the accuracy of the analytical method.

Materials

1. Telone, 99+% pure, obtained from Chem Service Inc.
2. Pentane, Reagent Grade.
3. Charcoal tubes.
4. 10 ul and 25 ul Microsyringes
5. Glassware. Wash all glassware with soap and water and rinse with deionized water, followed by a pentane rinse.

Safety Precautions

1,3-Dichloropropene is irritating to skin, eyes, and mucous membranes. Avoid skin contact. Avoid breathing vapors. Use only in a well ventilated area, preferably under a fume hood. Wear rubber gloves and protective clothing.

Standards Preparation

5 mg/ml Stock: Weigh 125 mg of 99% Telone and dissolve in 25 ml of pentane.

1 mg/ml Stock: Weigh 50 mg of 99% Telone and dissolve in 50 ml of pentane.

Record the concentration of both standards.

Sample Preparation

Prepare six audit samples from the stock standards according to the following table:

Sample	1 mg/ml Std	5 mg/ml Std
1	5 ul	0 ul
2	5	0
3	0	5
4	0	5
5	0	20
Blank	0	0

1. Break off the inlet end of the sample tube.

2. Insert the syringe needle into the charcoal bed of the primary section of the tube, and slowly inject the appropriate volume of spiking solution. Do not allow the liquid to run down the sides of the tube.

3. Cap the open end of the tube with the plastic cap provided.

4. Assign a random number to each sample, keeping track of the concentrations. Label each tube with its assigned number and store at 4°C until ready for analysis.